# VIBRONIC STRUCTURE OF THE $NO_3$ $\tilde{X}\ ^2A_2'$ SYSTEM

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The $\tilde{X}\ ^2A_2'$ state of $NO_3$ under jet cooled conditions is investigated via laser induced fluorescence ( LIF ) and two-color resonant four-wave mixing ( 2C-R4WM ) techniques. The electronic structure of $NO_3$ is thought to be similar to that of $BF_3$, and the latter has been well documented in the literatures[ab]. The $BF_3$ highest occupied molecular orbital ( HOMO ) possesses peculiar electronic structure with orbital localization on each of three F's and no contribution on the center atom, B. For $NO_3$, the HOMO corresponds to a singly occupied molecular orbital ( SOMO ), and, in the $\tilde{X}\ ^2A_2'$ state ( $\tilde{A}\ ^2E''$ and $\tilde{B}\ ^2E'$, too ) of $NO_3$, the un-paired electron is localized on the three O's and has no contribution on N. For this state, the degenerate vibrations are naturally expected to strongly affect the electron motion, which can be referred to as "degenerate-vibrationally induced vibronic coupling" on the non-degenerate electronic state. The SOMO characteristics of $NO_3$ have been confirmed by high-level quantum chemical computation[c]. The characteristic features of the vibrational structure of the $\tilde{X}\ ^2A_2'$ state may possibly be understood by the vibronic coupling. One feature is an unexpectedly large spin splitting of $1_0$ ( = $N_K$ ) of the $3\nu_4$ ($a_1'$) level observed by 2C-R4WM[d], and this splitting can be understood as the good quantum number behavior of $P$ ( $= K_v + \Sigma = \Lambda + l + \Sigma$ ) derived from the coupling.

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